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Original article

Near infrared spectroscopic studies on coatings of 19th century wooden parquets from manor houses in South-Eastern Poland

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ABSTRACT

The floor in a building is an integral part of the interior and is usually considered as a very valuable component of decoration. The flooring style, construction, manufacturing technologies, finishing and maintenance reflects local traditions, available resources and craftsmanship. Traditional techniques of parquet surface finishing were used in manor houses of South-Eastern Poland until the 1st half of the 20th century. Unfortunately, the major part of historical wooden parquets was irreversibly destroyed due to the introduction of collective property and the expropriation of manor houses after World War II. It is necessary to develop the knowledge related to the chemical, physical and mechanical properties of antique floor heritage, for its proper conservation. Near infrared spectroscopy was applied here for rapid and non-destructive recognition of natural finishes traditionally applied for the protection of the wooden floors. The system was capable to correctly identify the reference finishes applied on contemporary wood samples. However, analyses of antiques floors were more problematic. The set of samples of original antique decorative wooden flooring was collected from manor houses in Tarnowiec and Falejówka. Both houses contained well preserved wooden flooring that had not been subject to restoration in the past. The method shows great potential, even if in some cases an ambiguous classification was obtained. The reasons included natural deteriorations of floors during service life. Originally used substances might change their chemical composition during lifetime as a result of aging, weathering, usage and external contaminations. Given that, it was concluded that the results of spectroscopic evaluations might provide valuable assistance to conservators and facilitate decisions on the proper object maintenance.

1. Research aims

Proper conservation of original architectural surface is vital to meet the concept of authenticity of the cultural heritage. The wood finishing technique and the varnish application methodology strongly affects the parquet performance and its conservation. The knowledge of varnish composition and degradation stage can therefore essentially support decisions about appropriate maintenance and restoration procedures. The objective of this work was to assess the suitability of near infrared spectroscopic analysis for identification of the coating substances applied on antique parquets as surface finishing. The possibility of identification of the surface degradation degree due to ageing, environmental influences and handling was also investigated. The other task was to establish a spectral database of natural substances frequently used in 19th century for wooden floors coating. Methodology and chemometric models developed within the framework of this research might serve for identification of the substances that were applied to the parquets. Finally, near infrared spectroscopy may be also a useful technique for assessment of the chemical changes to the wooden surfaces before and after the floor restoration.

2. Introduction

The wooden parquet flooring was introduced in France in the first half of the 17th century. One of the earliest and most famous examples of parquet flooring on the territory of Poland is situated in Łańcut Castle, where floors were constructed in the second half

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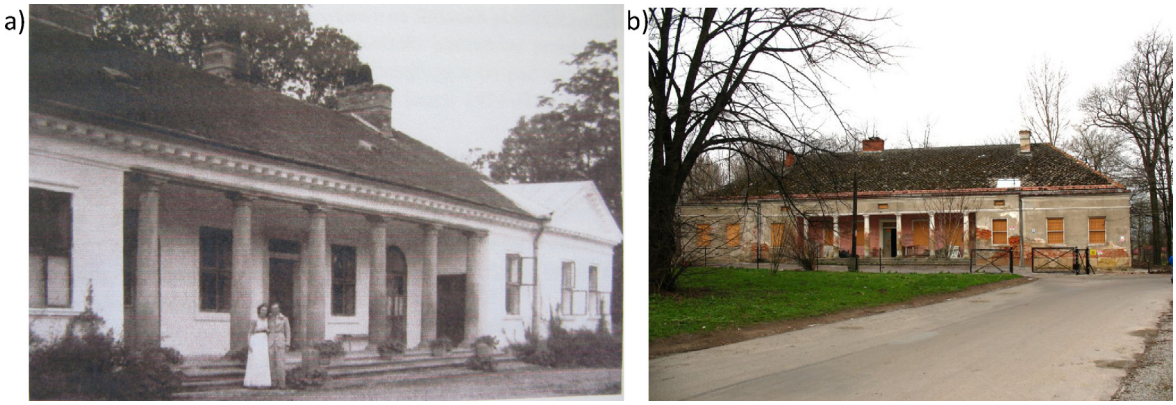

Fig. 1. Tarnowiec manor house at the beginning of XX century (a) and now (b).

of the 18th century [1]. The wooden parquets researched within this study belong to the manor houses in Tarnowiec and Falejówka, both located near Łańcut. The Tarnowiec manor house was built in ~1830 (Fig. 1). The building was partially destroyed during World War II and rebuilt in 1952. All the changes did not affect the interior layout of the house on the garden side. Hence, original wooden flooring set with beams placed on a layer of sand is still preserved [2].

The current state of the Falejówka manor house is dated at "1924", probably referring to the last structural renovation. The building served as a primary school after the World War II. Since the 1980s, the building has been abandoned and unfortunately partially ruined due to problems related to leaking roof and lack of a rainwater drainage system. Nevertheless, on the garden side, oak tile flooring is still preserved in some of the rooms. The structure and design of parquet in Falejówka is similar to that of Tarnowiec manor houses.

One-layer plank parquets structure made from a solid wood was most frequently applied in antique palaces and manor houses of South-Eastern Poland (Fig. 2a). Construction details of most parquets were rather simple as well as the geometric patterns of tiles. Sand, wedges or wood shavings were usually applied as a base. The bottom surface of typical 19th century parquets was usually uneven (Fig. 2b). Therefore, supplementary elements, made of small wood pieces, chips or sand, were deposited under the parquet in order to support its base.

Historical craftsman techniques of floor installation and finishing were used in antique buildings in Poland until the first half of the 20th century. The parquet had to be placed evenly and well levelled, that individual parquet elements could not have any gaps, uneven points, cracks, indentations or spallings. Wooden parquets were sanded with a hand scraper along the fibres after posing the floor. The wood surface was locally wetted with hot water in order to simplify smoothing work. Finally, the parquet was usually sanded with steel shavings.

There were several natural substances that could be used for wood surface protection [3], even if wax and oil varnish were traditionally the most popular for wooden parquet finishing. Depending on the technical characteristics the oil-based varnish penetrates the wood surface impregnating it to a certain depth. The impregnation depth of wax is usually smaller, but the advantage is that wax fills the natural pores of the wood structure. It should be mentioned here that, in order to increase the penetration depth, both wax and varnish were applied on the floor surface after heating up the product by boiling it in hot water.

Varnishing with the use of vegetable oils is the oldest known method of surface finishing. Vegetable oils, especially linseed oil, tung oil and colophony are hydrophobic, resistant to leaching, non-toxic and might be used as plasticizers. Linseed oil is chemically considered as a complex mixture of glycerol esters, mainly unsaturated fatty acids [4]. Process of wood varnishing consists of repeated soaking with hot varnish until full saturation of the wood surface. Thanks to its properties, such as formation of continuous film with good optical and mechanical characteristics, linseed oil was extensively used as a medium also for paintings since the 15th century.

Waxing was also frequently used as a finishing method of antique wooden parquets, as well as in furniture making, since

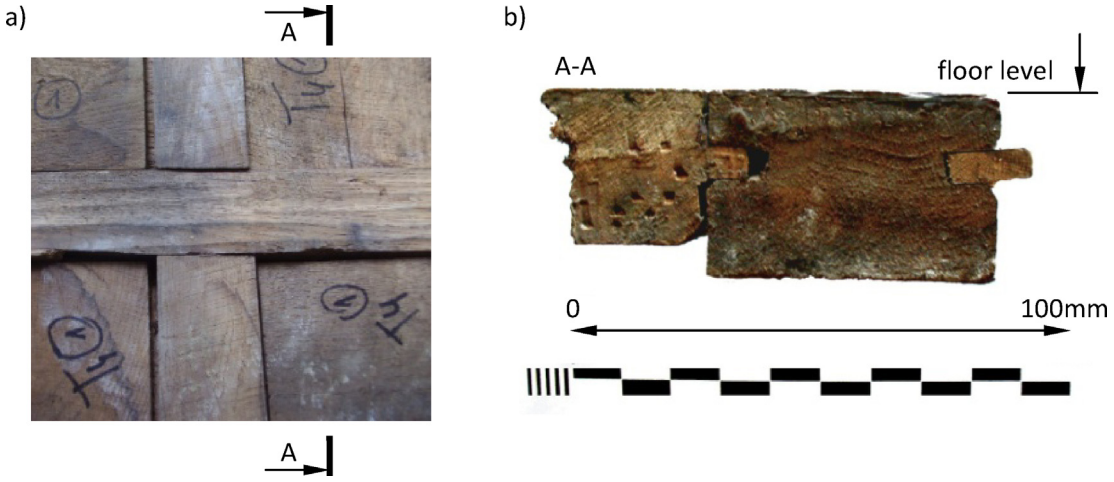

Fig. 2. Uneven bottom side of a Tarnowiec parquet tile (a) and example of differences in thickness between the frame and the filling (b).

the baroque era. Waxes, beeswax and paraffin are resistant to moisture, reversible, non-toxic and resistant to most organic solvents. Unfortunately waxes accumulate dust, are sensitive to heat and mechanical scratches and might become darker in time [4]. Chemically beeswax includes more than 300 components, including: monoesters (~35%), hydrocarbons (~14%), free acids (~12%), diesters (~14%), hydroxyl polyesters (~8%), hydroxyl monoesters (~4%), triesters (~3%), acid polyesters (~2%), acid monoesters (~1%) and other unidentified components (~7%) [5]. Wax bars were pressed against the surface and rubbed into the wood by polishing with a piece of felt. The temperature of wood rose as a result of rubbing and friction. In consequence it was possible to penetrate the wood surface with the melted wax. A hybrid use of varnish and wax was also used in order to take advantage of both coatings. Moreover, even if floors were originally varnished with vegetable oils, wax was commonly used during periodic maintenance of the floor [6]. Dedicated pastes for the cleaning and protection of wooden parquets, were introduced to the market after World War II. These contained mixture of wax and paraffin, dissolved in volatile organic solvents such as turpentine, gasoline or BTEX and were applied without raising the temperature directly on the floor. Lately, synthetic oils (derivatives of petroleum) became most popular in the conservation of wooden parquets.

Most studies focusing on traditional wood finishing have been devoted to the identification of varnishes on historical musical instruments [7,8]. Unfortunately, little attention has been paid to the identification of wooden floor's finishing. The first analytical study of archaeological beeswax was performed by Kühn in 1960 [9], using infrared spectrometry. Gas chromatography was suggested by Popescu et al. [10] as a method to certify the presence of linseed oil in old paintings. Mazzeo et al. [11] proposed X-ray analysis (SEM-EDX), X-ray diffraction, pyrolysis-gas chromatography–mass spectrometry for characterization of the inorganic pigments composition and the binding media from paint samples. Generally, techniques requiring micro-sampling of varnishes are used to elucidate the layers structure as well as to analyse the chemical composition of the finishing substances [12].

Recently available, noncontact, non-destructive and in situ techniques are very much favoured to assist the assessment and the conservation of cultural heritage objects [13]. Simplicity and short time of measurement provide the possibility of numerous repetitions, which significantly increase the reliability and accuracy of data. Fourier transform near infrared (FT-NIR) spectroscopy is proposed here for characterization of wooden floors, due to its potential on-site application, allowing completely non-destructive, fast and repeatable measurements. The objectives of this work were:

- to assess the suitability of FT-NIR for identification of the coating substances applied on antique parquets as surface finishing;
- to create a spectral database of natural substances frequently used in 19th century for wooden floor's coating;
- to develop chemometric algorithms suitable for identification of parquet coatings;
- to test the novel classification procedures on the original antique samples collected in two manor houses.

3. Experimental study

3.1. Antique wood samples

The samples from Tarnowiec manor house were collected from rooms #1, #4 and #5 (Fig. 3). The parquet samples in Falejówka were collected from the floor of the Living Room.

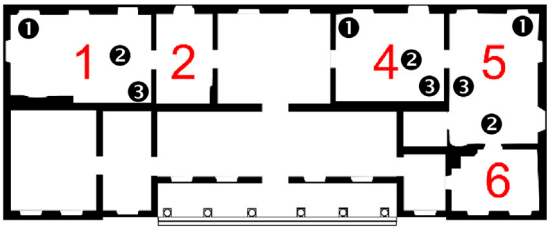

Fig. 3. Plan of Tarnowiec manor house with numbered rooms and parquet sampling positions; external corner ❶, communication path ❷ and internal corner ❸.

Parquet samples were taken from three locations in each room: the corner of the room close to external walls, the corner of the room close to internal walls and the traffic/walking path zone. The investigated floors were very dirty and in some places had severe mechanical damage. Sporadically, biological decay on the bottom side of panels was detected. For all the samples used for laboratory investigations only superficial infestation was allowed. Surface of each sample was therefore carefully refreshed (sanding by hand) in order to remove thin layer of dirt and to assure evenness of the surface. Liquid cleaning was not used in order to avoid any interaction of solvents with investigated surfaces. Samples were conditioned in a climatic chamber to standard climate conditions ($\pm 20\,^{\circ}C, \pm 60\%$ RH) before testing. The wood species used for antique floors included:

- oak (*Quercus* sp.) in case of panel parquet from the Falejówka manor house;
- oak (*Quercus* sp.) or oak (*Quercus* sp.) in combination with elm (*Ulmus minor* Mill.) in case of parquets from the Tarnowiec manor house

General information of investigated samples is summarized in Table 1. Chemical composition of samples was previously reported by Różańska et al. [2]. Photos and technical sketches of investigated floors are presented on Fig. 4a and b and on Fig. 4c for Tarnowiec, and Falejówka manor houses, respectively.

3.2. Contemporary wood samples

Two wood species corresponding to that of investigated antique parquets [oak (*Quercus* sp) and elm (*Ulmus* sp)] were selected as contemporary reference specimens. The wood samples originated from the same region of Poland as the historic floors. The set of reference wood pieces was chosen considering wood density, growth ring width, and anatomical structure. Finally, wood of small to medium ring width, with RT (mixed radial and tangential) sections and with pith position on the bottom side was selected. The contemporary wooden boards were cut into samples of dimensions $100 \times 100 \times 25\,mm^3$ (width × length × thickness, respectively). The surface of samples was finished before applying the coatings by three-stage sanding with a paper grit of P50, P100 and P150. The sanding was performed manually to avoid any chemical changes of wood surface that may occur as a result of elevated temperature occurring during mechanical processing. The surface topography obtained corresponded therefore to that of the investigated ancient parquet.

Part of the contemporary wood samples was coated with varnish (98% linseed oil and 2% siccatives) and natural beeswax. Preparation and application of coatings followed traditional technology [14,15]. Penetration depth was investigated by means of color reaction as described in standard [16]. Reagent prepared from 1 g Sudan Black (Sudan III) and 10 g of finely ground chalk ($CaCO_3$) was applied on the smooth cross section of coated wood. It was stained pale pink color in the zone saturated with varnish/wax. The

Table 1
Summary for sampling and properties of investigated antiques floors.

Location	Room #	Basement presence	Floor structure	Wood species	Sampling point	Comments
Falejówka	–	No	Empty space + beams + boarding	Oak (*Querus* sp.)	Whole room	Cracks in the wood not exceeding the depth of 6 mm, heavy organic and mineral contamination, surface mycelium of *Serpula lacrymans*, signs of *Xestobium rufovillosum* infestation
Tarnowiec	1	Yes	Sand + joists + boarding	Oak (*Querus* sp.)	External corner	No signs of decay, heavy organic and mineral contamination, surface mycelium of *S. lacrymans*, mould fungi mycelium
					Communication	No signs of decay, surface mycelium of *S. lacrymans*
					Internal corner	No signs of decay, heavy organic and mineral contamination, surface mycelium of *S. lacrymans*
	4	No	Sand + joists	Oak (*Querus* sp.)	External corner	Cracks in the wood not exceeding the depth of 10 mm, heavy organic and mineral contamination, small mycelium of *Antrodia sinuosa*, signs of *X. rufovillosum* infestation
					Communication	No signs of decay, heavy organic and mineral contamination, surface mycelium of *S. lacrymans*, mould fungi mycelium
					Internal corner	Cracks in the wood not exceeding the depth of 10 mm, heavy organic and mineral contamination, small mycelium of *A. sinuosa*, signs of *X. rufovillosum* infestation
	5	No	Sand + joists	Oak (*Querus* sp.) + Elm (*Ulmus minor* Mill)	External corner	Cracks in the wood not exceeding the depth of 10 mm, heavy organic and mineral contamination, signs of *X. rufovillosum* infestation
					Communication	Cracks in the wood not exceeding the depth of 5 mm, heavy organic and mineral contamination, small mycelium of *A. sinuosa*, signs of *X. rufovillosum* infestation
					Internal corner	No signs of decay, organic and mineral contamination, small mycelium of *A. sinuosa*

sample remained dark gray in the not saturated zones. The depth of penetration of the wax/oil in the wooden samples was measured visually with magnifying glass (Brinell). The accuracy of depth estimation was ± 0.1 mm. Sixty contemporary oak and elm samples were finally prepared. Any further characterization and measurement was carried out 5 months after the application of the finishes, in order to assure proper maturation/drying of coatings. Samples were conditioned in a climatic chamber to standard climate conditions (± 20 °C, ± 60% RH) before testing.

3.3. FT-NIR measurement

Both contemporary and historical samples were measured by using FT-NIR spectrometer VECTOR 22-N produced by Bruker Optics GmBH. The instrument was equipped with a standard fiber-optic probe (N 228-z, made of quartz) and germanium-diode detector, and used the thermoplastic resin Spectralon as a reference. The spectral resolution of the spectrophotometer was 8 cm^{-1}, and spectral range was 4000–12000 cm^{-1}. The spectral wavenumber interval was 3.85 cm^{-1} with zero-filling = 2. Each spectrum was computed as an average of 32 successive scans. Five separate spectra were measured on each sample, assuring careful selection of the measurement location and elimination of any sources of uncertainties. All measurements were performed in controlled climate conditions (± 20 °C, ± 60% RH).

3.4. Data analysis

OPUS 6.5 (Bruker Optics GmBH) has been used for signal processing and data analyses. Spectra preprocessing included computation of the second derivative with the Savitzky-Golay algorithm. Near infrared spectra interpretation, in regard to wood, oil and wax, was performed according to literature [17–21] and the band assignments used are presented in the Table 2.

In this research cluster analysis (CA), principal component analysis (PCA), Identity test (IT) and Quick Compare test (QC) were applied, for discrimination of FT-NIR spectroscopic data [22,23].

4. Results and discussion

4.1. Analysis of contemporary wood

The measured penetration depth of varnish (oil) in oak wood was varying between 0.75 and 2.9 mm, where in the case of wax the depth was in the range between 0.4 and 2.0 mm. Measurements of the penetrations depth in elm samples were more problematic, due to peculiar anatomical structure and low wood porosity, compared to oak. The average penetration depth was finally estimated to ~ 2 mm and ~ 1 mm for oily varnish and wax respectively. It was shown, therefore, that both oil and wax penetrated contemporary oak samples more easily than elm.

The preparation of spectral database of all investigated species/coatings was the foremost step for the analysis of historical parquets. The entire set of natural wood, as well as coated samples was scanned and evaluated with FT-NIR. The most varying parts of the coated and no-coated woods spectra are presented on Fig. 5. The band interpretation was based on the literature references (Table 2). Each original reflectance peak of the NIR spectra appears in the second derivate as a valley in the same wavenumber (light wavelength). Moreover, two phantom peaks are generated beside the source peak due to derivative calculation procedure.

Some apparent variations within presented spectra can be noticed, which indicate differences in chemical composition of investigated surfaces. Even if spectra of oak and elm woods coated with wax and varnish have rather similar shapes (with respect to coating type); several band shifts as well as some peaks additional to those of the natural wood are clearly discernible in the coated samples. It is especially noticeable in regions 4200–4400 cm^{-1}, 5600–5900 cm^{-1} and 7100–7300 cm^{-1}. The series of spectral peaks

Table 2
Band assignment of FT-NIR spectra of wood and visual assignment of signals derived by coatings.

	Wavenumber, cm^{-1}		Polymer assignment	Functional group	Experiment			Reference
	Literature	Experiment			Wood	Wax	Varnish	
1	4100	4100	Wax	CH	x	x	x	[19]
2	4198	4198	Wax/lignin	CH	x	x	x	[19,20]
3	4261	4265	Oil	CH_2		x	x	[17]
4	4283	4289	Cellulose, hemicellulose	CH	x			[20]
5	4323	4319	Wax	CH_2		x		[18]
6	4340	4337	Oil	CH_3			x	[17]
7	4401	4412	Cellulose, hemicellulose	CH, CH_2, OH, CO	x	x	x	[20]
8	4686	4678	Hemicellulose/lignin/extractives/oil	CH, C=C, C=O, CO + CH_2	x	x	x	[17,20]
9	4739	4750	Cellulose	OH	x	x	x	[20]
10	4808	4809	Cellulose semicrystalline and crystalline	OH, CH	x	x	x	[20]
11	5219	5219	Water	OH		x	x	[20]
12	5219	5222	Water	OH	x			[20]
13	5464	5457	Cellulose semicrystalline and crystalline	OH, CO	x	x	x	[20]
14	5587	5581	Oil	OH			x	[21]
15	5593	5593	Cellulose semicrystalline and crystalline	CH	x	x		[20]
16	5664	5664	Wax	CH_2		x		[18]
17	5700	5681	Oil	CH_2			x	[17]
18	5776	5792	Wax	CH_2		x		[18]
19	5790	5800	Oil	CH_2			x	[17]
20	5800	5806	Hemicellulose (furanose/pyranose)	CH	x			[20]
21	5872	5875	Cellulose	CH			x	[20]
22	5872	5887	Cellulose	CH	x	x		[20]
23	5963	5959	Lignin	CH	x	x	x	[20]
24	5995	5993	Extractives	CH	x	x	x	[20]
25	6286	6286	Cellulose crystalline	OH	x	x	x	[20]
26	6472	6472	Cellulose	OH	x	x	x	[20]
27	6800	6800	Hemicellulose (glucomannan)	OH	x	x	x	[20]
28	7003	6985	Amorphus cellulose/water	OH	x	x	x	[20]
29	7163	7158	Not assigned (aliphatic chains)	CH	x			[21]
30	7173	7173	Wax	CH		x		[19]
31	7194	7185	Oil	CH_3			x	[21]
32	7321	7309	Cellulose	CH	x	x	x	[20]
33	7410	7410	Hemicellulose/all	CH	x	x	x	[20]

FT-NIR: Fourier transform near infrared.

present in the above regions are mostly assigned to -CH stretching and -CH_2 stretching/deformation of combination bands and overtones of fundamental vibrations. These are, according to literature [17–19], characteristic of natural finishes, such as beeswax or linseed oil. The presence of beeswax is revealed in the mid infrared region (IR) as aliphatic -CH and -CH_2 (absorptions at 2910 cm^{-1} and 2842 cm^{-1}), as well as in the region of the carbonyl bond (~1734 cm^{-1}). It is in agreement with its chemical composition since beeswax contains aliphatic esters with long carbon chains, free wax acids and hydrocarbons [24]. Visual analysis of FT-NIR spectra confirmed the presence of several unique spectral bands appearing exclusively in oil varnished (signals 6, 14, 17, 19, 21 and 31) and/or wax-coated samples (signals 5, 16, 18 and 30). More details regarding visual spectra interpretation is summarized in Table 2. It was possible, consequently, to assume that FT-NIR spectroscopy is capable of characterizing finished wood surfaces, and it may be used for identification of coatings applied on wood.

Spectra of all samples investigated were used for preparation of chemometric models. Firstly, cluster analysis (CA) was prepared for each species and finish. The validation of model was realized by means of test set previously extracted from the spectra database. The validation set was then compared with developed models by means of Cluster Analysis Test [22]. All spectra of validation set were accurately identified (100% success rate).

PCA was secondly performed in order to confirm effectiveness of CA. As a result, shown on Fig. 6, spectra were evidently separated into three distinguished groups according to the type of surface finishing. Spectra were preprocessed by means of 2nd derivative + vector normalization and analyzed in three regions containing the highest spectral differences (4200–4400, 5600–5900 and 7100–7300 cm^{-1}). Computed selectivity *S*, in case

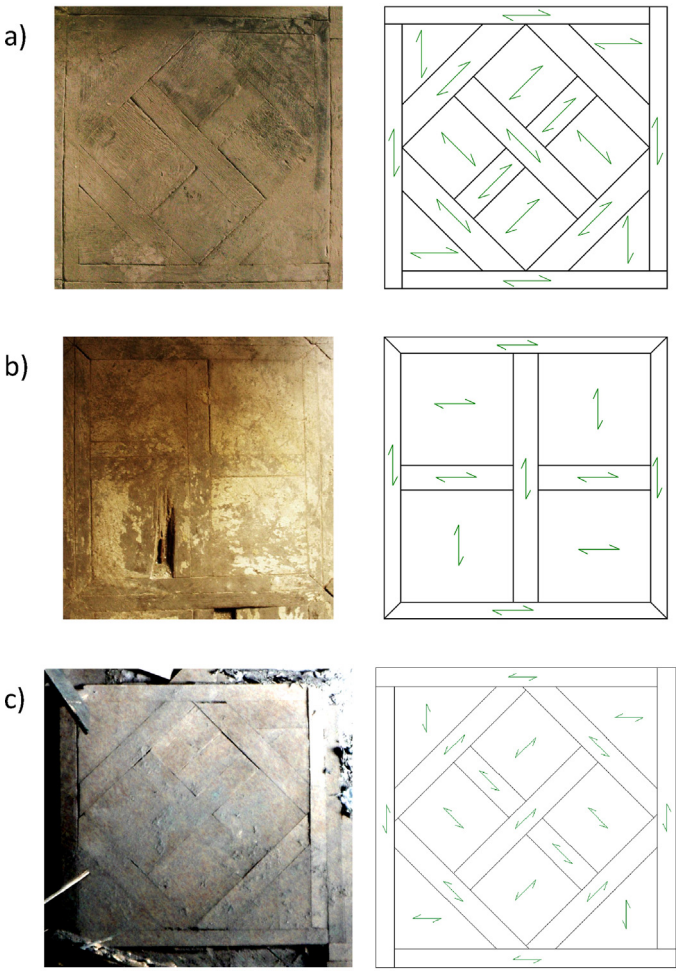

Fig. 4. Picture (left) and design schema (right) of parquets from Tarnowiec manor house; oak floor from room #4 (a), elm/oak floor from room #5 (b), and oak floor from Falejówka (c). Note: arrows indicate fibre directions of wooden elements.

of natural wood, was > 1; which shows clear separation between coated and no-coated samples. It was also observed that PCA scores computed from coated samples varied significantly. In both oak and elm natural wood, the data points cloud is relatively dense and formed unique cluster. However, the distribution of points corresponding to wax and varnish, as shown on Fig. 6, followed almost linear trend. It was an effect of different quantity of varnish/wax deposited on wood surface (due to natural wood heterogeneity, varying porosity and permeability). The direction of arrows indicates the increase of the spectral distance due to increase of the coating (varnish and/or wax) concentration (coating/wood mass ratio). A clear tendency is noticed therefore on Fig. 6, where coated samples follow a spread along PC2/PC3 for varnish, and PC3 for wax. Concluding, PCA confirms suitability of FT-NIR spectroscopy for wood finishes identification, having in the same time further potential for the quantitative analysis.

4.2. Analysis of antique floors

4.2.1. Falejówka manor house floor

FT-NIR spectra of antique floors samples were measured and analyzed, in parallel to contemporary samples. No apparent differences, as previously observed in case of contemporary wood, were noticed for samples of antique floors from Falejówka. It was assumed by means of visual assessment that spectra of antique parquet wood and contemporary no-coated wooden samples were almost identical. None of any spectral peaks characteristic for oil and/or wax was noticed in the FT-NIR spectra. Also the other identification models described above (CA, IT and QC) did not detect any trace of substances possibly used in the past for parquet finishing. An example of the clustering of the unknown coating sample collected from the wooden floor in Falejówka is shown on Fig. 7. The spectrum of antique sample was located within the natural oak cluster, possessing also very low heterogeneity index (high spectral similarity). Evaluation results of the chemometric tests for all the antique floor samples are summarized in Table 3. Concluding, no evidence of oil, wax or any other substance was found on the samples from Falejówka.

4.2.2. Room #1 of Tarnowiec manor house floor

The set of samples collected from room #1 of the Tarnowiec manor house were, in contrast to Falejówka samples, apparently more suspected to be retaining some of the coating substances. It was due to the peculiar smell of the wood and also a haptic impression. Some clear evidences of peak characteristics of wax were observed even by visual assessment in the FT-NIR spectra. A synthesis of all identification results is shown in Table 3, where it can be seen that, the most frequent chemical substance detected was wax. It should be mentioned, however, that 16 spectra were classified by means of cluster analysis as varnish-coated. Identity test detected wax presence in more than half of the spectra, while, no unique identification (selectivity $S > 1$ in case of more than one reference group) was possible in 39 spectra (within the set of 90); where natural wood together with wax-coating identifications were obtained.

Finally, combining results from visual spectra assessment with IT and QC test, it was concluded that, the finish used on the analyzed floor was wax.

It was also found that the sampling position within the room influenced success of coating identification. FT-NIR spectra of more than half samples taken from the internal corner of the room contained peaks characteristic of wax. On the contrary, only 9 spectra from communication path and just 2 spectra from external corner contained similar spectral features. Analogous results were obtained by means of QC test, even if number of wax-identified samples was lower than that of IT. No presence of finishing substance was detected in samples originated from external corner in the case of QC test. It is clear that the traffic within different zones of the house, and even within each room, is not uniform and in some zones might result in excessive use of the flooring material. Indeed, it was evident by examining raw floor samples after their collection from manor houses. Samples from the communication part of the floor showed excessive abrasive degradation, in contrast to those collected from internal corners. Another factor that might have affected identification results is related to the preparation of samples. Indeed, FT-NIR measurements required preliminary sanding of the surface to assure dirt-free measurement area. During this operation, it could also be possible that part of the original coating was unintentionally removed.

4.2.3. Room #4 of Tarnowiec manor house floor

No presence of varnish coating was detected in room #4 of Tarnowiec manor house. Only few spectra were identified as being different from natural wood and most of these were collected from the external corner of the room. The identified coating in that corner was always wax. The identification was based on: visual observation (1 spectrum), CA test (5 spectra), IT (8 spectra) and QC test (1 spectrum).

In analogy to observations from room #1, for all the samples from the traffic zone (communication path) it was not possible to detect any presence of finish. Nevertheless, 63 of 90 spectra were not uniquely identified in IT ($S > 1$ for natural wood and wax-coated

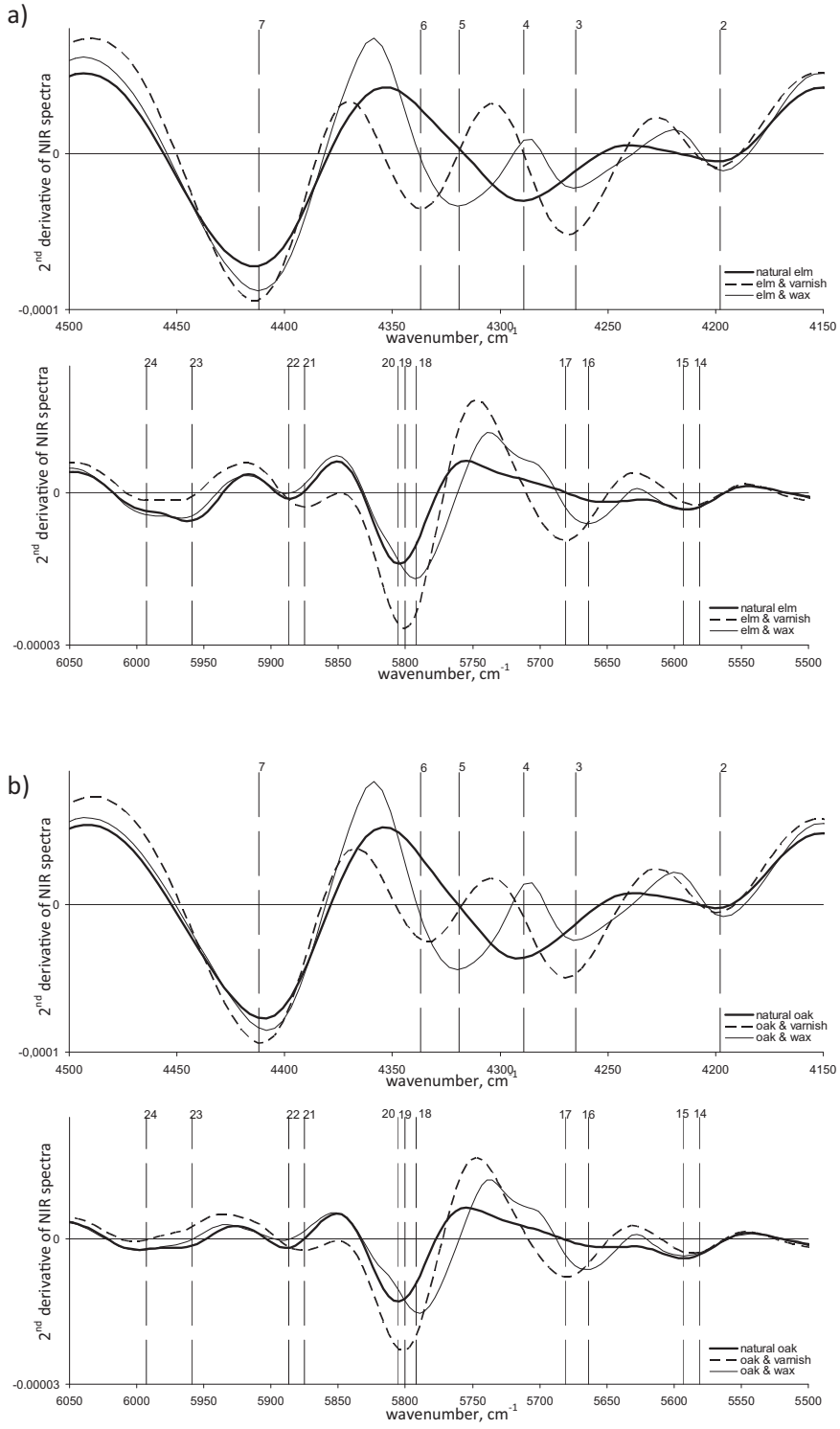

Fig. 5. Second derivative spectra of natural and finished elm (a) and oak (b) contemporary woods.

clusters) suggesting some traces of wax in the wooden samples. The less certain samples were those collected in internal corner of the room #4, where only CA test and IT identified a few spectra as wax-coated.

4.2.4. Room #5 of Tarnowiec manor house floor

Elm wood samples were studied from the floor of the room #5 of Tarnowiec manor house. As it was already mentioned, the impregnation capability of elm wood is lower than that of oak. Therefore less finishing substances are expected to be deposited on the surface of elm floor. In consequence, only in a few samples some presence of coating was detected with FT-NIR. One spectrum from external corner of the room #5 was classified as wax-including (positive results in both CA test and IT). All chemometric algorithms identified wax presence in some samples originated from communication path. Approximately 30% of samples were identified as wax containing by means of CA and IT in the internal part of the room #5.

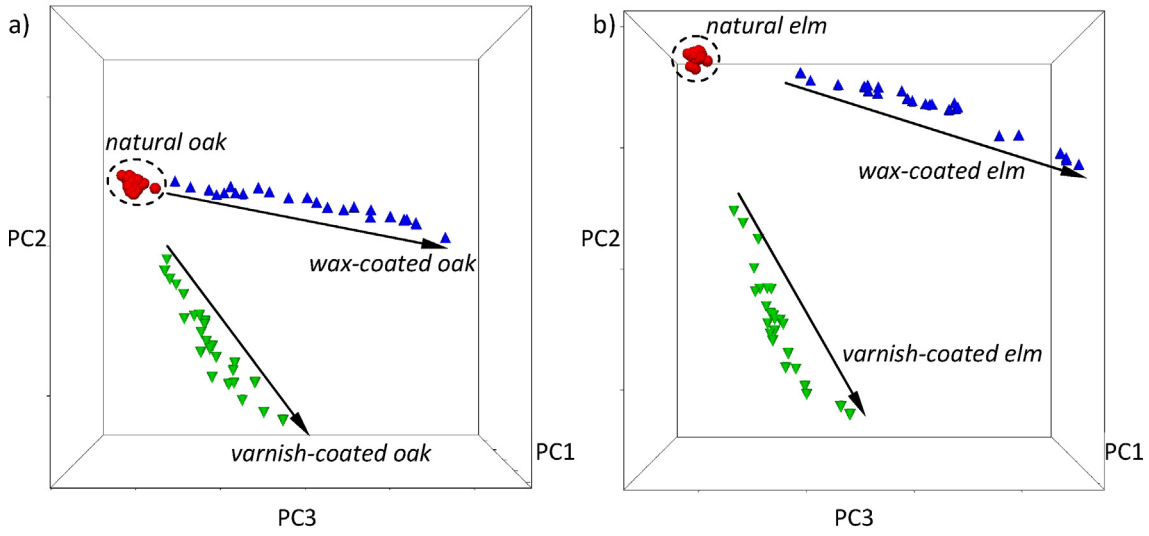

Fig. 6. Principal components analysis of Fourier transform near infrared spectra of oak (a) and elm (b) wood coated with wax and varnish.

4.3. Factors limiting coating identification on ancient wooden floors by means of FT-NIR

4.3.1. Similarity between natural wood, varnish- and wax-coated FT-NIR spectra

The method presented here is based on the measurement of the invisible infrared spectra from the surface of complex natural polymers composite. Even if all such polymers are chemically different, their infrared spectra are relatively similar. It was shown here that some of the distinctive spectral features (peaks assigned uniquely to wax and/or varnish) may be successfully used for coating identification of the freshly finished wooden surfaces. However, the possible modifications of the chemical components, as discussed below, may change the FT-NIR spectra and make identification more problematic.

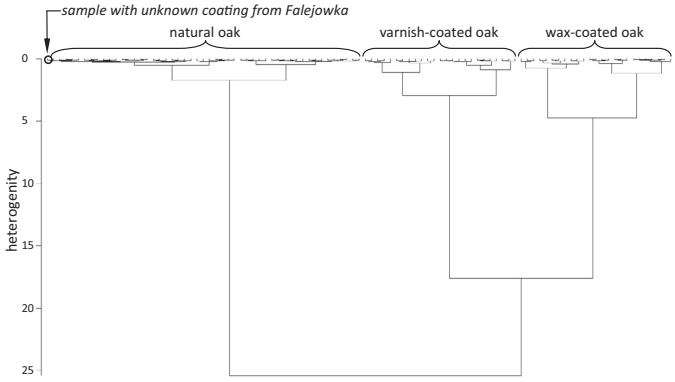

Fig. 7. Cluster analysis test of oak samples from Falejówka manor house.

4.3.2. Mathematical algorithms used for identification

Several mathematical algorithms for spectra interpretation were tested within this study. It is clear that each algorithm possesses advantages and limitations. As a result, slightly different detection rate has been noticed for each method (Table 3). The proper selection of the due spectra preprocessing and identification method is therefore crucial. Similar conclusions were presented by Jurado-Lopez and Luque de Castro [25] for detection of substances used for paintings.

4.3.3. Contamination of the floor surface during service life

The floor is probably the part of the interior of a house most exposed to deterioration, contamination and devastation. It is necessary to properly maintain its surface by applying detergents, protection products or even to refurbish the surface by sanding the outer layer and applying new protective coatings. It was impossible to record or reconstruct all the maintenance activities during the service life of wooden floors from Falejówka and Tarnowiec manor houses. It was only assumed by visual and bibliographical

Table 3
Results of identification of investigated samples by means of visual spectra assessment and selected chemometric methods.

Species	Location	Room	Place	Number of spectra (out of 30) with track of peaks related to							
				Visual assessment		Cluster Analysis test		Identity test		Quick Compare test	
				Wax	Varnish	Wax	Varnish	Wax	Varnish	Wax	Varnish
Oak	Falejówka	–	Whole room	0	0	0	0	0	0	0	0
	Tarnowiec	1	External corner	2	0	10	0	16	0	0	0
			Communication	9	0	14	5	19	0	7	0
			Internal corner	18	0	11	11	16	0	14	0
		4	External corner	1	0	5	0	8	0	1	0
			Communication	0	0	0	0	1	0	0	0
			Internal corner	0	0	4	0	7	0	0	0
Elm		5	External corner	0	0	1	0	1	0	0	0
			Communication	3	0	10	0	13	0	3	0
			Internal corner	1	0	11	0	11	0	0	0

inventory that non-significant activities (such as floor replacing) were undertaken in the past.

4.3.4. Sample preparation

It is necessary to properly prepare the sample surface before FT-NIR measurement. The three phase sanding was selected here in order to assure removal of the exterior dirt layer and unify surface smoothes (to minimize an effect of light scatter). Such methodology is therefore a compromise between preserving the original state of the sample and assuring proper conditions for FT-NIR measurements.

4.3.5. Weathering and deterioration of coatings

Finally, the finish identification success depends also on the capability of the applied technique to identify features related to the time-dependant deterioration and weathering of the coating substances. Deterioration of coatings includes several processes and depends on chemical stability of coatings themselves as well as on environmental factors. The most common degradations involve changes of the polymeric chains; coatings might become more cross-linked/polymerized, or conversely, broken down/depolymerized.

The chromatographic profile of ancient beeswax presents significant differences to that of contemporary beeswax. Even if contemporary beeswax presents a well recognizable pattern of n-alkanes, its degradation mechanism is still unclear. According to Regert et al. [26], the most stabile components are esters, even though they are partially hydrolyzed, forming palmitic acid and long-chain even-numbered alcohols. Degradation caused by bacteria is theoretically responsible for the decrease of hydrocarbons in wax.

Drying and ageing processes of varnish-coated objects are also very complex [7]. The hardening of linseed oil is due to its auto-oxidation followed by a polymerization. In the presence of natural antioxidants the oil has tendency to formation of peroxidic compounds. The polymerization is related to formation of cross-linked structures by intermolecular coupling of radicals from unstable peroxide groups by the formation of C—C, C—O—C, C—O—O—C bonds between the fatty acid chains [27,28]. On a following phase, the labile cross-links are changing to highly stable network, which still contains unreacted triglycerides and low molecular weight molecules. A film of linseed oil becomes touch-dry in a few days, but the drying reactions continue for many years. After years of natural ageing a further progressive oxidation is observed. Hence, the chemometric models developed for freshly coated surfaces might be not always general enough to be able to clearly recognize the same substances after natural weathering.

5. Conclusions

FT-NIR spectroscopy was used in this research for identification of the wood surface coatings applied on the antique parquet floors from two manor houses in Poland. Such technique possesses important advantages and has a great potential for assisting research on historical objects as well as for their conservation. The technique is non-destructive, rapid and accurate, allowing measurements in the lab and also in the field. The most important limitation of FT-NIR is rather difficult interpretation of the spectra and complex data mining. The series of chemometric methods presented here might be, however, an example of successful application of FT-NIR in cultural heritage research.

FT-NIR spectroscopy was capable of perfectly identifying surface finishes applied on contemporary reference samples. It was a stimulus for trials with historic samples. Unfortunately, it was impossible to identify the original parquet coating in case of Falejówka manor house samples. The presence of wax surface finishing was however detected in the parquets collected from Tarnowiec manor house.

Several factors might affect success of the coating identification:

- the current state of the object (deterioration, damage, weathering);
- the history of maintenance during service life (including renovations, cleanings, fire events, flooding, etc.);
- sample collection and preparation (selection of wood samples from no-traffic paths, proper climatic conditioning, surface preparation);
- FT-NIR spectra preprocessing and data mining (scanning conditions, derivative, smoothing, averaging, chemometric methods, validation of models, etc.).

It can be concluded, nevertheless, that properly used FT-NIR spectroscopy can be a new useful tool in routine work of researchers and technicians dealing with the assessment and conservation of these valuable architectural surfaces.

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